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IN SULFURIC ACID AEROSOLS: COMPARISONS BETWEEN HYDROCARBON
AND FLUOROCARBON ALCOHOLS

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13. ABSTRACT (Maximum 200 words)

Heterogeneous reactions of gas phase molecules with aqueous sulfuric acid aerosols play a significant role in the destruction of ozone in the stratosphere. These processes include the acid-catalyzed reactions of HCl and HBr with ClONO₂ (BrONO₂) and HOCl (HOBr) to generate photoactive halogen molecules, particularly in colder regions of the stratosphere where they are more soluble in the water-rich aerosols. Our objective is to determine the mechanisms and rate-limiting steps of reaction of these atmospheric gases with these supercooled sulfuric acid droplets. By employing molecular beam scattering techniques, we probe the nature of the initial gas-sulfuric acid collision and the immediate fate of HCl and HBr molecules trapped at the acid's surface as they either desorb into the gas phase or react in the interfacial or bulk regions of the aerosol. In this interim grant period, we have explored the ability of organic molecules dissolved in sulfuric acid to form surface films that impede gas uptake and thereby reduce the rates of heterogeneous reactions in the acid. These surface-active organic molecules are found naturally in the upper troposphere and tropopause and may be produced in the exhaust of jet aircraft. We have so far investigate the entry of trifluoroethanol and HCl gas molecules into bare sulfuric acid and acid coated with butanol, dodecanol, and hexadecanol. These hydrocarbon surfactants have kept us busy, and we have not yet compared them with fluorocarbon ones.

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2. Objectives

Heterogeneous reactions of gas phase molecules with aqueous sulfuric acid aerosols play a significant role in the destruction of ozone in the stratosphere. These processes include the acid-catalyzed reactions of HCl and HBr with ClONO_2 (BrONO_2) and HOCl (HOBr) to generate photoactive halogen molecules, particularly in colder regions of the stratosphere where they are more soluble in the water-rich aerosols. Our objective is to determine the mechanisms and rate-limiting steps of reactions of these atmospheric gases with these supercooled sulfuric acid droplets. By employing molecular beam scattering techniques, we probe the nature of the initial gas-sulfuric acid collision and the immediate fate of HCl and HBr molecules trapped at the acid's surface as they either desorb into the gas phase or react in the interfacial or bulk regions of the aerosol.

In this interim grant period, we have explored the ability of organic molecules dissolved in sulfuric acid to form surface films that impede gas uptake and thereby reduce the rates of heterogeneous reactions in the acid. These surface-active organic molecules are found naturally in the upper troposphere and tropopause and may be produced in the exhaust of jet aircraft. We have so far investigated the entry of trifluoroethanol and HCl gas molecules into bare sulfuric acid and acid coated with butanol, dodecanol, and hexadecanol. These hydrocarbon surfactants have kept us busy, and we have not yet compared them with fluorocarbon ones.

3. Status of Effort

We have used molecular beam scattering to explore the entry of trifluoroethanol and HCl into 60 and 70 wt % D_2SO_4 at 213 K, concentrations that are typical of the low and mid latitude stratosphere. The acid is prepared in three ways: 1) pure acid containing only D_2O and D_2SO_4 (no surfactant), 2) sulfuric acid pre-mixed with the soluble surfactants butanol at 0.2 M or dodecanol at 0.002 M, or 3) sulfuric acid dosed with the insoluble surfactant hexadecanol from an effusive doser in vacuum.

We chose butanol because it freezes at 188 K, below the 213 K temperature of our experiments, and because it is among the most prevalent alcohols in the troposphere and

tropopause. Our surface tension measurements show that a 0.2 M butanol solution in 70 wt % sulfuric acid at 213 K generates a surface that is more than 80% coated with butanol. Dodecanol freezes at 297 K and appears to induce freezing in the supercooled acid at concentrations above 0.002 M; it was chosen because it is a soluble surfactant that should be pack more tightly and impede gas uptake more thoroughly than butanol due to its much longer hydrocarbon chain, even at lower bulk concentrations of 0.002 M. Hexadecanol freezes above 322 K and is dosed onto the surface in vacuum to avoid freezing. Hexadecanol is the most studied insoluble surfactant on water; well-formed monolayers impede water evaporation by factors of up to 10,000.

Trifluoroethanol ($\text{CF}_3\text{CH}_2\text{OH}$) was chosen as a model protic gas that undergoes $\text{H} \rightarrow \text{D}$ exchange upon entering deuterated sulfuric acid. Trifluoroethanol is a basic molecule and is rapidly protonated by sulfuric acid, leading to $\text{H} \rightarrow \text{D}$ exchange. Those $\text{CF}_3\text{CH}_2\text{OH}$ molecules that thermalize upon collision with the surface but do not enter the acid remain as $\text{CF}_3\text{CH}_2\text{OH}$. Because $\text{CF}_3\text{CH}_2\text{OH}$ is weakly soluble in 70 wt % D_2SO_4 at 213 K, all dissolved trifluoroethanol molecules evaporate rapidly after entering the acid. The $\text{CF}_3\text{CH}_2\text{OH} \rightarrow \text{CF}_3\text{CH}_2\text{OD}$ exchange fraction, monitored by mass spectroscopy, is therefore equal to the fraction of impinging molecules that enter the acid and become available for reaction with other solute species. The same principles apply to HCl , an acidic gas that is a major repository for Cl atoms in the stratosphere.

4. Accomplishments and New Findings

During this interim period, we made four new findings:

- 1) We first used argon atom scattering to detect the presence of hydrocarbon molecules at the surface of sulfuric acid. Argon atoms scattering from bare, 60 and 70 wt % D_2SO_4 at 213 K lose less energy and thermalizes less often than when they scatter from acid doped with a surfactant. This is because the hydrocarbon chains of the alcohol surfactants create a very rough interface that enforces multiple collisions and extensive energy transfer. We now exploit this observation to confirm the existence of the surfactant at the surface of the acid before each experiment.

2) Trifluoroethanol undergoes nearly complete H→D exchange with 60 and 70 wt % D_2SO_4 at 213 K. The measured exchange fraction of 0.95 implies a nearly unimpeded entry into the acid. This high entry rate was expected, based on the basicity of the alcohol and the protonating power of the acid. However, to our great surprise, a 0.2 M butanol solution reduced the trifluoroethanol H→D exchange fraction from 0.95 to only 0.89. This small change indicates that a nearly complete butanol monolayer, whose existence is confirmed by argon scattering and by surface tension measurements, does *not* significantly impede the transport of the trifluoroethanol into the acid. A similar reduction was observed for 0.002 M dodecanol. Our original expectation was that the exchange fraction would decrease from 0.95 to ~0.2 or lower as the butanol or dodecanol molecules covered 80% or more of the surface. We hypothesize that the CF_3CH_2OH molecules reside long enough on the surface of the supercooled acid to diffuse into the bulk through fluctuating holes between the butanol or dodecanol molecules. Alternatively, the CF_3CH_2OH may react with interfacial D_2SO_4 or D_3O^+ that lie between the alcohol chains. A small reduction in the exchange fraction from 0.95 to 0.79 was also observed when using sodium dodecyl sulfate, an even longer soluble surfactant. We tentatively conclude that soluble surfactants do not impede organic molecules from entering supercooled sulfuric acid and therefore should not alter heterogeneous reaction rates in the tropopause or upper troposphere.

3) We next deposited the insoluble surfactant hexadecanol on 70 wt % D_2SO_4 using an effusive doser within the vacuum chamber. Upon depositing one monolayer of hexadecanol, we observed no change in the H→D exchange rate for trifluoroethanol and no change in the evaporation rate for water. The water evaporation rate was reduced by 25% only when we deposited many hundreds of hexadecanol monolayers. In this case, we think that the hexadecanol froze and coalesced so quickly that the surface was not actually coated with the surfactant. Indeed, at very high dosing rates, the deposited hexadecanol could be viewed by eye to freeze into small clumps within the acid. We regard these first experiments with insoluble surfactants as tentative at the moment.

4) The most important measurement we have made is the H→D exchange fraction of HCl in 0.2 M butanol solutions in 60 wt % D₂SO₄ at 213 K. We observed that the exchange fraction *increased* from 0.5 for the bare acid to 0.7 for the butanol-covered acid. This result was entirely unexpected, but it appears to be reproducible. We hypothesize that the butanol molecules act like water to dilute the sulfuric acid, effectively generating a weaker acid solution. We have previously observed that the exchange fraction for HCl increases as the acidity concentration is lowered, as the more dilute solutions provide more interfacial water molecules that the HCl can protonate. However, assuming that butanol acts like water, the addition of 0.2 M butanol to 60 wt % D₂SO₄ corresponds to a decrease in acidity from 60.0 wt % to only 59.6 wt %, with an expected increase in the H→D exchange fraction from 0.50 to 0.52. This 0.02 difference is small in comparison to the measured 0.2 increase in the exchange fraction. One explanation is that the actual concentration of butanol in the interfacial region is much higher than in the bulk, as our surface tension measurements indicate. The acid would therefore be more dilute at the surface than in the bulk, creating an interfacial region where HCl may readily find a water molecule to protonate before it evaporates. Within this picture, the barrier properties of the surfactant would be superceded by the dilution effect it creates. We are testing this idea by measuring the HCl → DCl exchange fraction as a function of bulk butanol concentration. The implication of this result is surprising: it indicates that surfactants may actually facilitate the transport of HCl into sulfuric acid aerosols rather than hinder it!

5. Personnel Supported by AFOSR Funding

This interim grant provides funding for two graduate students:

- 1) Jennifer Lawrence is in her fifth year of graduate school. She is the lead person in charge of the surfactant studies.
- 2) Sam Glass is in his fourth year of graduate school. He is presently assisting Jennifer in the surfactant studies and will begin a new research project soon exploring the ways in which the H→D exchange rates change as a function of acid temperature.

6. Publications

No papers were published during this interim period. However, we hope to collect enough data soon to publish the surfactant studies, particularly in regard to the surprising results for increased HCl uptake in surfactant-coated sulfuric acid.

7. Interactions/Transitions from June 1 through August 31, 2002

a. Invited and Contributed Talks and Posters about AFOSR-Sponsored Research

1) Invited talk at Telluride Conference on Chemical and Optical Properties of Atmospheric Aerosols, August, 2002

2) Invited talk at the American Chemical Society National Meeting, Symposium on Frontiers in Atmospheric Chemistry, August, 2002

b. No consultative functions during this interim period.

c. No transitions to technological applications during this interim period.

8. New Discoveries, Inventions, Patent Disclosures During the Interim Period

No patented inventions or patented disclosures.

9. Honors/Awards during the Interim Period

The PI was elected as a fellow of the American Physical Society during this interim period, in part for his work on studies of heterogeneous reactions in supercooled sulfuric acid.